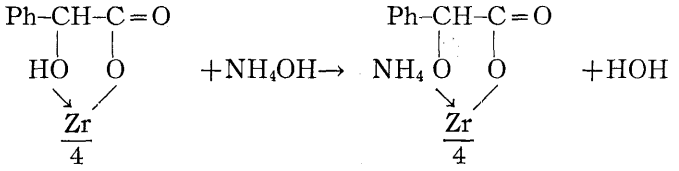
REACTION BETWEEN ALPHA-METHOXYPHENYLACETIC ACIDS AND ZIRCONIUM

JOSEPH J. KLINGENBERG AND RICHARD J. THEIS
Chemistry Department, Xavier University, Cincinnati, Ohio

Mandelic acid, *p*-chloro- and *p*-bromomandelic acids are recognized reagents for the gravimetric determination of zirconium. Some doubt exists as to the nature of the precipitate formed between zirconium and these reagents. Kumins (1947), the discoverer of the reaction, believed that the compound formed with mandelic acid was a simple salt, i.e., $Zr(C_8H_7O_3)_4$. Feigl (1949), however, proposed a chelate-type structure to explain the solubility of zirconium mandelate in aqueous ammonia. Feigl supposed that complexation enhances the acidic character of the hydroxyl hydrogen in mandelic acid to such an extent that it is capable of being replaced by ammonium ion to form the ammonium salt.

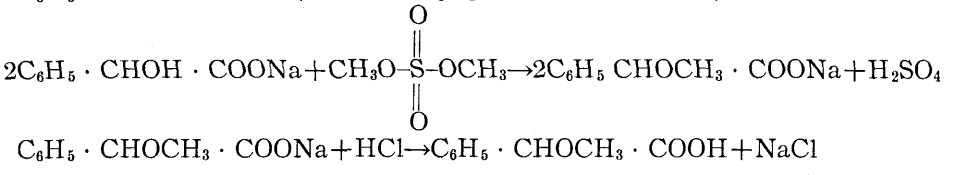


Some evidence as to whether or not this is so could be obtained by replacing the hydroxyl hydrogen in mandelic acid with a methyl group, i.e., by synthesizing α-methoxyphenylacetic acid and testing its reaction with zirconium ion. The methyl group would be expected to be less labile than the original hydrogen and possibly to interfere with the formation of the zirconium chelate. On the other hand it should not influence extensively the precipitation reaction, if the product is a simple salt.

This paper describes the preparation of α-methoxyphenylacetic acid and also the *p*-chloro- and *p*-bromo-derivatives and their testing for reaction with zirconium in solution.

Reagents

Alpha-methoxyphenylacetic acid was synthesized according to the procedure of Reeve and Christoffel (1950). One mole of mandelic acid was reacted with 13 moles of sodium hydroxide to form the sodium salt. To this was added slowly 5.5 moles of redistilled dimethyl sulfate to form the sodium salt of α-methoxyphenylacetic acid. The methylated and unmethylated salts were separated by crystallization from an acid solution of pH 3.1, the sodium salt of α-methyoxyphenylacetic acid being much less soluble at this pH. This sodium salt was then converted to the free acid by treatment with hydrochloric acid.



The acid was then extracted with ethyl ether and the ether was evaporated to give the solid acid. The *p*-chloro- and *p*-bromo- derivatives were synthesized in a

similar manner, starting with *p*-chloro- and *p*-bromo-mandelic acid. Results are given in table 1.

TABLE 1

Melting point (°C) and yields of methoxy acids

Name	Lit. mp	mp	% yield
α-methoxyphenylacetic acid	70–71	67–69	23
p-Cl-α-methoxyphenylacetic acid	85–86	84–85	36
p-Br-α-methoxyphenylacetic acid	95.5–97	96–96.8	24

Analytical Procedure

A zirconium solution calculated to be 0.05 M was prepared from recrystallized zirconyl chloride octahydrate. This was standardized by gravimetric analysis using mandelic acid, *p*-chloro- and *p*-bromo mandelic acids according to the procedures of Kumins (1947) and of Klingenberg and Oesper (1949). The results are given in table 2.

TABLE 2

Preparation of standard Zr solution

Reagent	ZrO_2 found
Mandelic Acid	.0586 gm
	.0588 gm
	.0588 gm
	.0585 gm
p-chloromandelic acid	.0590 gm
	.0590 gm
p-bromomandelic acid	.0590 gm
	.0590 gm
	Value Used .0590 gm

A 0.1 M solution of α-methoxphenylacetic acid was tested with the standardized zirconium solution. To a mixture of 10 ml of standard zirconium solution, 10 ml of concentrated hydrochloric acid, and 30 ml of water warmed to 65° C was added the 0.1 M α-methoxyphenylacetic acid. This approximates the conditions for the precipitation of zirconium with mandelic acid. No precipitate formed. Several other solutions containing less hydrochloric acid were run and precipitates containing zirconium appeared, but the zirconium oxide obtained on ignition did not correspond to the amount of zirconium added. The results appear in table 3.

When mandelic acid was added to the filtrate from two of the samples, a further precipitation of zirconium occurred. When this precipitate was added to the crucibles, burned, and the weight of residue added to the original, the total was only 0.0001 to 0.0004 gm from the standard. This indicated zirconium was definitely present in the original precipitate, otherwise the final results would have been high. The nature of the precipitate was further investigated.

The effect of ammonium hydroxide on the precipitate was studied since it dissolves the zirconium precipitate of mandelic acid to form the aforementioned complex. Upon addition of ammonium hydroxide to the system, the precipitate present appeared to dissolve. Further examination showed that zirconium

hydroxide was appearing. This indicates that the precipitate is not of the same type as that obtained with mandelic acid.

TABLE 3

ZrO^{++} vs. α-methoxyphenylacetic acid

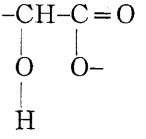
Amt. HCl used	Wt. Residue as ZrO_2
10. ml	0.0000 gm
5. ml	0.0168 gm
4.5 ml	0.0275 gm
3.5 ml	0.0276 gm
2. ml	0.0473 gm
	Amt. Added 0.0590 gm

Since the *p*-chloro- and *p*-bromo- derivatives were insoluble in water they were added as powder to a hot zirconium solution and stirred to form an emulsion. The solution became cloudy as a result of some of the acid oiling out but no zirconium precipitate appeared. Varying the pH also failed to precipitate zirconium with the *p*-chloro- and *p*-bromo- α-methoxyphenylacetic acids.

Discussion

From the evidence obtained in the experimental work with α-methoxyphenylacetic acids, it is apparent that the replacement of the alcoholic linkage of mandelic acid with an ether linkage definitely blocks the precipitation of zirconium. The zirconium binding force of the glycolic group, –CHOHCOOH, is completely destroyed when the methyl group is substituted and the sample is run at normal hydrochloric acid concentration of the mandelate method. The destruction of the zirconium—binding force may be due to both inductive effects and steric hindrance.

In the glycolic group,



both oxygens are negatively charged and form a precipitate with the positively charged zirconium ion quite easily. The hydroxyl hydrogen offers little or no blocking effect. However, when the methyl group is introduced in place of the alcoholic hydrogen, two new factors enter into the structural behavior of the acid. One is the fact that the methyl group is an electron donor, and helps satisfy the electronegativity of the adjacent oxygen atom. The ether oxygen thus formed is comparatively neutral, and no longer attracts zirconium ions. The other factor involves the blocking effect of the methyl group. This group, being much larger than the single hydrogen, would stearically hinder the formation of the zirconium chelate precipitate.

The fact, then, that α-methoxyphenylacetic acid and the *p*-chloro- and *p*-bromo- derivatives do not behave like mandelic acid and its *p*-chloro- and *p*-bromo- derivatives indicates that the mandelates are not simple salts, but are instead chelates.

Acknowledgment

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